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<b>(21) International Application Number:</b> PCT/US99/23154 <b>(22) International Filing Date:</b> 6 October 1999 (06.10.99)  <b>(30) Priority Data:</b> 9822654.1           17 October 1998 (17.10.98)   GB 9828816.0           31 December 1998 (31.12.98)   GB  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CRUICKSHANK, Graeme, Duncan [GB/GB]; 17 Wallington House, Belvedere Gardens, Whitley Road, Benton, Newcastle upon Tyne NE12 9PG (GB). WONG, Alfred, Tsz-Chun [GB/GB]; 217 Main Road, Sundridge, Sevenoaks, Kent TN14 6EJ (GB). STODDART, Barry [GB/GB]; 364 Durham Road, Low Fell, Gateshead NE9 5AP (GB).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ODOR-CONTROL METHODS AND COMPOSITIONS		
<b>(57) Abstract</b> <p>A method of controlling the odor of an animate or inanimate object comprising treating the object with a composition comprising an odor-control agent selected from large pore phosphate-containing molecular sieves having a pore diameter of at least about 5 Angstroms. The method and compositions used therein provide improved control of malodor.</p>		

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## ODOR-CONTROL METHODS AND COMPOSITIONS

### TECHNICAL FIELD

The present invention relates to odor-control agents, to the use thereof for controlling the odor of an animate or inanimate object, and to compositions containing agents for odor-control and for reducing malodor impression.

### BACKGROUND OF THE INVENTION

Effective odor control is an important objective in many consumer product applications designed for personal, household or institutional use, for example, fabric softening compositions, freshening compositions for fabrics and clothes, deodorant compositions for personal or household use, e.g., for deodorising pet, tobacco, cooking and toilet smells, personal cleansing compositions and cosmetics for controlling body odor, dentifrice and mouthwash compositions for controlling mouth odor, laundry compositions designed to clean and freshen fabrics, manual and machine dishwashing compositions for cleaning and deodorising dishes, plastic containers, etc., hard surface cleaning compositions for cleaning and deodorising floors, carpets and other floor coverings, bleaching compositions for fabric or household use. Odor control is also very important in many industrial situations, for example in rendering plants, spent grain dryers, pharmaceutical plants and cellulose pumping.

In general terms, odor can be described as the subjective perception of the sense of smell. Linnaeus's original classification of odors recognised that many odors are repulsive or nauseous in nature and by common agreement would be described as 'malodors'. Body fluids, for example, contain a variety of substances which are malodorous per se or which can over time form malodorous compounds by a fermentation or degradation mechanism, for example, volatile fatty acids (e.g. isovaleric acid), ammonia, amines (e.g. triethylamine), sulphur-containing compounds (e.g. mercaptans, sulphides), alcohols, ketones and aldehydes (e.g. furaldehyde). Apart from body fluids, there are many other potential environmental sources of malodors, e.g. tobacco and smoking, food and cooking

smells, pets, animal rendering, etc. In general, the object of odor control is to provide a process or composition that will give a more acceptable perception of smell, whether as a result of dilution, removal of the offending substance, or counteraction or masking, or indeed by preventing the generation of malodors at source.

One approach that has been taken to the control of gaseous odors involves absorption or adsorption of the odor on high surface area porous substrates such as activated carbon and zeolites. The known sorbents (which term includes both absorbents and adsorbents), however, have only a limited efficacy for odor-control and in particular are relatively poor sorbers of higher molecular weight and/or hydrophobic malodor components. In other words, the known sorbents have a relatively limited odor-absorption spectrum.

Accordingly, the present invention provides odor-control compositions and methods based on the use of odor-control agents which have a broader spectrum of odor absorption and which are significantly more efficient than known absorptive odor-control agents. The present invention also provides a range of consumer product applications which utilize the odor-control agents.

### SUMMARY OF THE INVENTION

In its broadest aspect, the present invention relates to the use of a large pore phosphate-containing molecular sieve having a pore diameter of at least about 5 Angstroms as agent for the control of odors.

Preferred odor-control agents herein are phosphate-containing molecular sieves selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn. Preferred are phosphate-containing molecular sieves having a pore diameter in the range from about 8 to about 15 Angstroms, especially preferred materials having a pore diameter greater than about 10 Angstroms, for example from about 11 to about 14 Angstroms.

The phosphate-containing molecular sieve odor control agents herein can also be used in combination with a non-phosphate molecular sieve, for example, a mesoporous molecular sieve having a pore diameter of at least about 13, preferably at least about 15, more preferably at least about 20 Angstroms.

Of these, highly preferred are the mesoporous molecular sieves designated M41S which consist essentially of crystalline, inorganic material exhibiting after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least 18 Angstroms. A highly preferred material under the M41S designation is MCM-41 which can be described as a mesoporous molecular sieve consisting essentially of inorganic, porous, crystalline material having, after calcination, a hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units.

In a method aspect, the present invention provides a method of controlling the odor of an animate or inanimate object comprising treating the object with a composition comprising an odor-control agent selected from large pore phosphate-containing molecular sieves having a pore diameter of at least about 5 Angstroms.

The present invention also provides an odor-control composition comprising an odor-control agent selected from large pore phosphate-containing molecular sieves having a pore diameter of at least about 5 Angstroms together with a carrier therefor. Such compositions can take various forms including particulate solids, liquids, gels and aerosols.

The present invention also provides a variety of consumer and retail products designed for personal, household, industrial and institutional use, for example, freshening compositions for fabrics and clothes, and odor-control and deodorant compositions for personal or household use, e.g., for deodorising pet, tobacco, cooking and toilet smells.

### **DETAILED DESCRIPTION OF THE INVENTION**

The compositions herein comprise a large pore phosphate-containing molecular sieve in an amount effective for controlling odors, preferably in an amount of at least about 0.001%, more preferably from about 0.001% to about 20%, and most preferably from about 0.05% to about 10% by weight of composition.

As used herein, the term "large pore molecular sieve" refers to a range of microporous and mesoporous crystalline materials built around an inorganic charged or neutral framework and possessing pores having a relatively uniform size distribution. In general, the pore diameter of the molecular sieves herein should be at least about 5 Angstroms. Preferred

herein, however, are large pore phosphate-containing molecular sieves having a pore diameter in the range from about 8 to about 15 Angstroms which can be used either alone or in combination with non-phosphate molecular sieves, for example those falling within the class of mesoporous materials wherein the pore diameter is at least about 13, more preferably at least about 15 and especially from about 20-200, more especially 30-100 Angstroms. Mesoporous molecular sieves of this type can be generally described as crystalline, inorganic materials which exhibit after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least about 18 Angstroms. As used herein, the term 'crystalline' indicates that the molecular sieve has sufficient order to provide, following calcination, a diffraction pattern such as, for example, by X-ray, electron or neutron diffraction with at least one peak. It should also be noted that the molecular sieve may exist as a mixture of physically distinct phases. Also, defects and imperfections can cause significant deviations from an ideal regular structure. Generally, however, the pore size distribution within a single phase will be within about 25%, usually within about 15% of the average pore size for that phase.

The pore diameter of the molecular sieves can be determined in known manner, for example, by transmission electron microscopy (TEM), x-ray diffraction or argon physisorption. TEM is the preferred technique herein. Suitable methods for determining pore diameter by argon physisorption are disclosed in US-A-5,098,684.

Molecular sieves suitable for use herein in combination with the phosphate-containing sieves include large pore natural and synthetic zeolites, i.e., molecular sieves based on a crystalline silicate or aluminosilicate framework. Large pore silicate molecular sieves (essentially aluminium-free) are also suitable for use herein. For a general discussion of zeolite-type molecular sieves, see D.W. Breck, *Zeolite Molecular Sieves, Structure, Chemistry and Use*, John Wiley & Sons, Inc., New York, 1974.

Molecular-sieves of the aluminosilicate variety (zeolites) can be represented by the empirical formula  $M_{2n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$ , where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, ammonium, magnesium, and calcium, n is the cation valence, and w represents the moles of water contained in the zeolitic voids. The zeolite framework is made up of  $SiO_4$  tetrahedra linked together by sharing of oxygen ions. Substitution of a Group IIIB metal such as Al for Si generates a charge imbalance, necessitating the inclusion of a cation. The structures contain channels or interconnected voids that are occupied by the cations and water molecules. The water

may be removed reversibly, generally by the application of heat, which leaves intact the crystalline host structure permeated with micropores that may account for >50% of the microcrystal's volume. In some zeolites, dehydration may produce some perturbation of the structure, such as cation movement, and some degree of framework distortion.

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There are two basic types of zeolite structures: one provides an internal pore system comprising interconnected cage-like voids; the second provides a system of uniform channels which, in some instances, are one-dimensional and in others intersect with similar channels to produce two- or three-dimensional channel systems. The preferred  
10 type has two- or three-dimensional channel systems to provide rapid intracrystalline diffusion in adsorption and catalytic applications.

Substitution of phosphorus for some or all of the framework silicon not only makes it possible to extend the range of molecular sieves to higher pore sizes but it also has  
15 significant impact on the residual framework charge, hydrophobicity, and the binding/complexing character of the molecular sieve.

Molecular sieves of the phosphate-containing class are well-known and are disclosed in a number of documents. Suitable aluminophosphates, for example, include those disclosed  
20 in US-A-4,310,440 and US-A-4,385,994. These aluminophosphates have essentially electroneutral lattices. US-A-3,801,704 discloses an aluminophosphate treated in a certain way to impart acidity.

An early reference to a hydrated aluminophosphate which is crystalline until heated at  
25 about 110 °C., at which point it becomes amorphous or transforms, is the "H<sub>1</sub>" phase or hydrate of aluminium phosphate of F. d'Yvoire, Memoir Presented to the Chemical Society, No. 392, "Study of Aluminium Phosphate and Trivalent Iron", July 6, 1961 (received), pp.1762-1776. This material, when crystalline, is identified by the JCPDS Internal Center for Diffraction Data card number 15-274. Once heated at about 110 °C.,  
30 however, the d'Yvoire material becomes amorphous or transforms to the aluminophosphate form of tridymite.

Compositions comprising crystals having a framework topology after heating at 110 °C or higher giving an X-ray diffraction pattern consistent with a material having pore  
35 windows formed by 18 tetrahedral members of about 12-13 Angstroms in diameter are disclosed in US-A-No. 4,880,611.

A naturally occurring, highly hydrated basic ferric oxyphosphate mineral, cacoxenite, is reported by Moore and Shen, *Nature*, Vol. 306, No. 5941, pp. 356-358 (1983) to have a framework structure containing very large channels with a calculated free pore diameter of 14.2 Angstroms.

Silicoaluminophosphates of various structures are disclosed in US-A-4,440,871, US-A-3,355,246 (ZK-21) and US-A-3,791,964 (ZK-22). Other disclosures of silicoaluminophosphates and their synthesis include US-A-4,673,559 (two-phase synthesis method); US-A-4,623,527 (MCM 10); US-A-4,639,358 (MCM-1); US-A-4,647,442 (MCM-2); US-A-4,664,597 (MCM-4); US-A-4,638,357 (MCM-5); and US-A-4,632,811 (MCM-3).

A method for synthesizing crystalline metalloaluminophosphates is disclosed in US-A-4,713,227, while an antimonophosphoaluminate and its synthesis are disclosed in US-A-4,619,818. US-A-4,567,029 discloses metalloaluminophosphates, while titaniumaluminophosphate and its synthesis are disclosed in US-A-4,500,651.

Other suitable phosphate-containing molecular sieves include the phosphorus substituted zeolites of CA-A-911,416; CA-A-911,417; and CA-A-911,418.

US-A-4,363,748 describes a combination of silica and aluminium-calcium-cerium phosphate as a low acid activity catalyst for oxidative dehydrogenation. GB-A-2,068,253 discloses a combination of silica and aluminium-calcium-tungsten phosphate as a low acid activity catalyst for oxidative dehydrogenation. US-A-4,228,036 discloses an alumina-aluminium phosphate-silica matrix as an amorphous body to be mixed with zeolite for use as cracking catalyst. US-A-3,213,035 teaches improving hardness of aluminosilicate catalysts by treatment with phosphoric acid. The catalysts are amorphous.

Other patents teaching aluminophosphates include US-A-4,365,095; US-A-4,361,705; US-A-4,222,896; US-A-4,210,560; US-A-4,179,358; US-A-4,158,621; US-A-4,071,471; US-A-4,014,945; US-A-3,904,550; and US-A-3,697,550.

Other pertinent references on phosphate-containing molecular sieves include S.T. Wilson and co-workers, *J. Amer. Chem. Soc.* 104, 1146 (1982); S.T. Wilson, B.M. Lok, C.A. Messina, and E.M. Flanigen, *ACS Symp. Ser.* 218, 79 (1983); B.M. Lok and co-workers, *J. Amer. Chem. Soc.* 106, 6092 (1984); U.S. Pat. 4,554,143; U.S. Pat. 4,567,029 S.T.



Wilson and E.M. Flanigen, ACS Symp. Ser. 398,329 (1989); and E.M. Flanigen, B.M. Lok, R.L. Patton, and S.T. Wilson, Pure & Appl.Chem.58,1351 (1986).

5 A number of specific synthetic routes to large pore phosphate-containing molecular sieves have been reported in the literature, for example,  $\text{AlPO}_4\text{-8}$  ( R.M. Dessau, J.L. Schlenker, and J.B. Higgins, Zeolites 10,522 (1990)); VPI-5 ( M.E. Davis, C. Montes, and J.M. Garces, ACS Symp. Ser. 398, 291 (1989)); cloverite (J. Patarin and co-workers, Proc. 9<sup>th</sup> Intern. Zeolite Conf. I, 263 (1993)); and JDF-20 (Q. Huo and co-workers, J. Chem. Soc., Chem. Commun. 875 (1992)). Cacoenite, a natural large pore ferroaluminophosphate  
10 has also been structurally characterised (P.B. Moore and J. Shen, Nature 306, 356 (1983)).

Of all the above, molecular sieves of the phosphate-containing type preferred for use herein include  $\text{AlPO}_4\text{-5}$ ,  $\text{AlPO}_4\text{-8}$ , SAPO-5, SAPO-37, VPI-5, Cloverite (an 18-membered ring gallophosphate), and JDF-20.

15 Another class of large pore molecular sieves suitable for use herein are the liquid crystal template-synthesised M41S range of mesoporous molecular sieves reported by C.T. Kresge and co-workers, Nature 359, 710 (1992) and by Beck and co-workers, J. Amer. Chem. Soc. 114, 10834 (1992). See also US-A-5,102,643, US-A-5,250,282, US-A-  
20 5,264,203, US-A-5,145,816, US-A-5,098,684, US-A-5,378,440, US-A-5,098,684, US-A-5,108,725 and US-A-5,057,296.

In general terms, the M41S mesoporous molecular sieves can be described (see US-A-5,378,440) as inorganic, porous, non-layered crystalline phase materials which exhibit,  
25 after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Angstrom Units with a relative intensity of 100 and a benzene adsorption capacity of greater than 15 grams benzene per 100 grams of anhydrous crystal at 50 torr and 25 °C.

30 Highly preferred M41S molecular sieves herein are mesoporous molecular sieves which consist essentially of inorganic, porous, crystalline material having, after calcination, a hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units. Such materials have been given  
35 the designation MCM-41 (see US-A-5,378,440).

Preferred molecular sieves for use herein have surface area of at least about 300 m<sup>2</sup>/g, more preferably at least about 400 m<sup>2</sup>/g and most preferred being at least about 500 m<sup>2</sup>/g. In addition, the molecular sieves preferred for use herein are relatively hydrophobic, being either aluminium-free or having an Si:Al molar ratio of at least about 10:1, preferably at least about 30:1, more preferably at least about 60:1, and especially at least about 100:1.

The molecular sieves can be used in colloidal or micron-sized form (with a primary particle size of less than about 10 microns, preferably less than about 1 micron, more preferably less than about 0.1 micron) or they can be used as larger sized particles ( spray-type compositions, for example, will generally have a particle size in excess of 10 microns) or they can be shaped or agglomerated into a wide variety of particle sizes. Generally speaking, shaped/agglomerated particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the molecular sieve can be extruded before drying or partially dried and then extruded.

It may be desirable to incorporate the molecular sieves with a binder or a porous matrix material or to use the molecular sieve in conjunction with another odor-control material. Suitable binders include inorganic materials such as sodium sulphate, clays, silica and/or metal oxides, such as alumina, titania, and/or zirconia. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels, including mixtures of silica and metal oxides. The clays may be naturally occurring clays, e.g., bentonite and kaolin. Suitable organic binders include cellulose derivatives such as carboxymethyl cellulose and water-soluble polymers such as sodium polyacrylate. Porous matrix suitable herein include silica-alumina, silica-magnesia, silica zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. Other odor-control agents suitable for use herein include small-pore zeolites such as Zeolite A, Zeolite X and Zeolite Y, activated carbon, charcoal and antimicrobial agents.

The odor-control agents herein can be utilised in a wide variety of product applications.

Odor-control and deodorant compositions according to the invention will generally comprise the odor-control agent in combination with a carrier therefor and/or a perfume.

In one aspect of the invention, such compositions are utilised to reduce malodor on inanimate surfaces such as carpets, upholstery, fabrics, clothes, etc., for example, clothes that have been stored for a long period of time, or carpets that have been contaminated with environmental odors such as food odors, tobacco odors, etc. Such compositions can thus be used to restore and/or maintain freshness by reducing malodor without the need for cleaning, washing or dry cleaning.

Preferred compositions of this sort take the form of a fluent or sprayable aqueous composition which in use is dispensed onto fabrics, clothes, carpets, shoe inners, etc. to restore their freshness by reducing malodor impression. The compositions are designed to extend the wear and freshness of the treated articles between cleaning, washing or dry cleaning. In the case of compositions which additionally contain a perfume, articles treated therewith will stay fresher longer, and receive extra freshening effect via perfume release.

Such compositions can also be supplemented by other conventional components of fluent and sprayable odor-control compositions. In preferred embodiments, the composition will comprise one or more of the following:

- a) from about 0.01% to about 1%, preferably from about 0.01% to about 0.5%, more preferably from about 0.015% to about 0.3% of perfume, preferably a perfume designed to present a freshness impression on a surface treated therewith. Suitably, the perfume contains a mixture of perfume ingredients selected from aromatic and aliphatic esters, alcohols, ketones, lactones, aldehydes, ethers, and condensation products of aldehydes and amines and is preferably essentially free from nitromusks and halogenated fragrance material. When high initial perfume odor impact is desired, it is also preferred to select a relatively hydrophilic perfume in which at least about 25% by weight of the perfume, more preferably about 50%, most preferably about 75%, is composed of perfume ingredients having a "calculated logP" (Clog P) of about 3 or smaller, Clog P being determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990);
- b) from about 0.1% to about 5%, preferably from about 0.2% to about 4%, more preferably from about 0.3% to about 3%, most preferably from about 0.4% to about 2% of water-soluble cyclodextrin odor-control agent, preferred cyclodextrins being selected

from alpha-cyclodextrin and derivatives thereof, gamma-cyclodextrin and derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. Suitable cyclodextrin derivatives for use herein include hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and  
5 hydroxypropyl beta-cyclodextrin. In compositions containing both cyclodextrin and perfume, the weight ratio of perfume to cyclodextrin is typically from about 3:100 to about 100:100, preferably from about 4:100 to about 50:100, more preferably from about 5:100 to about 40:100, even more preferably from about 5:100 to about 25:100, most preferably from about 1:8 to about 1:4;

10

c) from about 0.1% to about 10%, preferably from about 0.2% to about 7%, more preferably from about 0.3% to about 5% of a water-soluble metallic odor-control salt, preferably selected from zinc salts, copper salts and mixtures thereof, or of an astringent metallic salt such as the inorganic and organic salts of aluminium, zirconium, and zinc,  
15 and mixtures thereof. Particularly preferred astringent salts are the aluminium and zirconium salts such as aluminium halides, aluminium hydroxy halides, zirconyl oxide halides, and zirconyl hydroxy halides, and complexes of aluminium, zirconium, and/or zinc with amino acids, e.g., glycines.

20 d) from about 0.02% to about 3%, preferably from about 0.02% to about 3%, more preferably from about 0.05% to about 1%, most preferably from about 0.1% to about 0.3% of solubilizing aid for perfumes and/or other hydrophobic organic materials;

e) from about 0.0001% to about 0.5%, preferably from about 0.0002% to about 0.2%,  
25 more preferably from about 0.0003% to about 0.1% of a bactericide or preservative, preferred preservatives including Kathon<sup>®</sup> CG, Bronidox L<sup>®</sup>, Bronopol<sup>®</sup>, chlorhexidine, and its salts, e.g., with acetic and digluconic acids; Glydant Plus<sup>®</sup>, Germall II<sup>®</sup>, Abiol<sup>®</sup>, Unicide U-13<sup>®</sup>, Germall 115<sup>®</sup>, Nuosept<sup>®</sup> C, formaldehyde; glutaraldehyde; Cosmocil CQ<sup>®</sup>, Mikrokill<sup>®</sup>, dehydroacetic acid; and mixtures thereof;

30

Preservatives are especially preferred in compositions containing cyclodextrin to control microbial growth. It is preferred to use a broad spectrum preservative, e.g., one that is effective on both bacteria (both Gram positive and Gram negative) and fungi. Preferred antimicrobial preservatives are those that are water-soluble (at least 0.3g per 100 ml at  
35 room temperature) and are effective at low levels because the organic preservatives can form inclusion complexes with the cyclodextrin molecules and compete with the perfume

molecules for the cyclodextrin cavities, thus rendering the complexed preservatives much less effective.

f) from about 0.05% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.3% to about 3% of antistatic agent;

g) a liquid carrier inclusive of aqueous and non-aqueous carriers containing e.g., water, water-miscible organic solvents, hydrophobic liquids, propellants, etc in amounts generally from about 10 to about 99%, preferably from about 20 to about 75% by weight. Aqueous carriers are particularly suitable herein for the reduction of malodor impression. Preferred aqueous carriers contain water in at least about 50% by weight thereof and optionally contain an alcoholic solvent selected from low molecular weight monohydric alcohols (e.g., ethanol, methanol, or isopropanol), polyols (e.g. ethylene glycol or propylene glycol) and mixtures thereof, the alcoholic solvent preferably being in a level of less than about 5%, more preferably less than about 3%, and especially less than about 1% by weight of composition. Other suitable solvents include carbitol, acetone and dimethoxymethane.

The compositions of this invention can also contain a non-aqueous or hydrophobic liquid carrier. Suitable hydrophobic liquids include fatty acid and fatty alcohol esters, water-insoluble ethers and alcohols, polyorgano silicones, propellants and mixtures thereof. Such hydrophobic liquids are disclosed in US-A-4,053,851, US-A-4,065,564, US-A-4,073,880, US-A-4,278,655, and GB-A-2,018,590.

Preferred hydrophobic liquids include volatile silicone oils. As used herein, "volatile" refers to those materials which have a measurable vapor pressure at ambient conditions. Such volatile silicone oils may be cyclic or linear. A description of volatile silicone oils is found in Todd, et al., "Volatile Silicone Fluids for Cosmetics", 91 Cosmetics and Toiletries, 27-32 (1976). Preferred volatile silicone oils include those having from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 5 silicon atoms. Examples include: Dow Corning 344, Dow Corning 345 and Dow Corning 200 (sold by Dow Corning Corporation); 7207 and 7158 (sold by General Electric Company); and SWS-03314 (sold by SWS Silicones Corporation).

Propellants, e.g. propane, n-butane, isobutane, etc., are used generally in an amount from about 10% to about 95%, preferably from about 20% to about 70%, of the total composition;

- 5 h) from about 0.1% to about 15%, preferably from about 1% to about 8% of a suspending, thickening or gelling agent. Suspending agents suitable herein include the clays and hydrophobically-treated clays such as those based on montmorillonite clays, e.g., bentonites and hectorites. Many such clay suspension agents are commercially available. They include, for example, Bentone 38, Bentone 34, Bentone 27, Bentone 14, and  
10 Bentone LT sold by NL Industries, Inc., and Tixogel (bentonite) sold by United Catalyst, Inc. The clay minerals are made hydrophobic by treating them with a cationic surfactant material. A preferred cationic surfactant is a quaternary ammonium cationic surfactant. A particularly preferred cationic surfactant is ditallow dimethyl ammonium chloride (e.g., quaternium-18). The suspension agent can also be used in conjunction with an activator  
15 such as propylene carbonate, ethanol, and mixtures thereof.

Suitable thickening agents include polymeric thickeners such as carboxymethyl cellulose, methyl cellulose, hydroxypropylmethylcellulose, sodium polyacrylate and polyethylene powder, such as Microthene.RTM. powder, a polyethylene powder manufactured by  
20 U.S.I. Chemicals (New York, N.Y., USA), having a mean particle diameter of less than about 20 microns.

Other optional components for use herein include defoaming agents, antifoaming agents, bacteriocides, fungicides, insect and moth repelling agents such as pheromones,  
25 citronellol, citranellal, citral, linalool, cedar extract, geranium oil, sandalwood oil, 2-(diethylphenoxy)ethanol, 1-dodecene, etc., colorants, especially bluing agents, antioxidants, and emollients including esters such as isopropyl myristate and isopropyl palmitate; alcohols such as lauryl alcohol, hexadecyl alcohol, and oleyl alcohol; carboxylic acids such as lauric and oleic acid; lanolin and its derivatives such as  
30 acetylated lanolin, paraffins such as the mineral oils and water-insoluble non-volatile polyalkyl and polyaryl siloxane gums and fluids, and mixtures thereof.

The compositions of the present invention can be incorporated in an article of manufacture comprising the composition plus a liquid, spray or pump dispenser. The  
35 spray dispenser can be any of the manually activated devices for producing a spray of liquid droplets as known in the art, e.g. trigger-type, pump-type, non-aerosol self-

pressurized, and aerosol-type spray devices, as well as electrodynamic spray devices. It is preferred that at least about 80%, more preferably, at least about 90% of the droplets have a particle size of larger than about 30 $\mu$ m.

- 5 The odor-control compositions herein can be used by distributing, e.g., by placing the aqueous solution into a dispensing means, preferably a spray dispenser and dispensing an effective amount onto the desired surface or article. An effective amount as defined herein means an amount sufficient to absorb odor to the point that it is not discernible by the human sense of smell yet not so much as to saturate or create a pool of liquid on said  
10 article or surface and so that when dry there is no visual deposit readily discernible. Distribution can be achieved by using a spray device, a roller, a pad, etc.

Household surfaces that can be treated herewith include countertops, cabinets, walls, floors, bathroom surfaces and kitchen surfaces. Household appliances that be treated  
15 herewith include refrigerators, freezers, washing machines, automatic dryers, ovens, microwave ovens, dishwashers, garbage cans, waste disposal units etc. Fabric and/or fabric articles that can be treated herewith include clothes, shoes, curtains, drapes, shower curtains, upholstered furniture, carpeting, bed linens, bath linens, tablecloths, sleeping bags, tents, car interior, e.g., car carpet, fabric car seats, etc. Other items that can be  
20 treated herewith include cat litter, pet bedding, pet houses and household pets themselves.

Odor-control composition components suitable for use herein are described in more detail in the Appendix to the Description (Ref: ODC1L)

25

All percentages, ratios, and parts herein are by weight unless otherwise stated.

#### Examples

In the examples, the following abbreviations are used:

30	DC345	Cyclomethicone available from Dow Corning
	IPM	Isopropyl myristate
	Clay	Quaternium 18 hectorite
	DC200	Dimethicone (20cs) available from Dow Corning
35	Carbonate	Propylene carbonate
	Propellant	Propane/isobutane

HPCD

Hydroxypropyl beta-cyclodextrin

Examples I-VI

5

The following illustrates examples odor-control compositions of the present invention suitable for use as aerosol deodorants or freshening compositions. The molecular sieve samples have the following pore diameters: VPI-5 - 12 Angstroms; Cloverite - 13 Angstroms; JDF-20 - 15 Angstroms; AIPO4-5 - 8 Angstroms; MCM-41 - 35 Angstroms.

10 All levels are in % by weight of composition.

	I	II	III	IV	V	VI
VPI-5	-	-	-	10	-	-
Cloverite	-	-	4	-	-	4
JDF-20	-	10	-	-	-	-
AIPO4-5	5	2	-	-	8	-
MCM-41	8	-	-	-	1	4
HPCD	-	-	-	-	1	-
DC345	20	15	25	15	25	20
IPM	6	5	-	5	-	7
Clay	1.2	1	0.8	1.5	0.5	1.1
DC200	4	2	3	4	-	5
Carbonate	0.4	0.3	0.2	0.3	0.1	0.2
Propellant	----- To 100 -----					

15 The compositions are prepared as follows. The silicone materials materials are added to a batch tank, followed by the IPM and clay, and then mixed for 10 minutes with a rotary mixer. The carbonate is added and the mixture is mixed for an additional 5 minutes. The molecular sieve is added and the mixture is mixed for another 10 minutes. Any remaining ingredients are then added and the mixture mixed for a further 5 minutes. The liquid

20 batch is finally milled under high shear conditions to form a concentrate. The concentrate is then added to a standard aerosol can, the propellant is added under pressure and the can sealed.



When sprayed onto inanimate or animate surfaces, the compositions provide improved malodor control .

### Appendix to the Description

#### Perfume

- As used herein, perfume includes fragrant substance or mixture of substances including
- 5 natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein.
- 10 Typically, perfumes are complex mixtures of a plurality of organic compounds.

Suitable perfumes for use herein preferably contain ingredients selected to provide a 'freshness' impression on the surface to which the composition is applied.

- 15 Preferably, at least about 25%, more preferably at least about 50%, most preferably at least about 75%, by weight of the perfume is composed of fragrance material selected from the group consisting of aromatic and aliphatic esters having molecular weights from about 130 to about 250; aliphatic and aromatic alcohols having molecular weights from about 90 to about 240; aliphatic ketones having molecular weights from about 150 to
- 20 about 260; aromatic ketones having molecular weights from about 150 to about 270; aromatic and aliphatic lactones having molecular weights from about 130 to about 290; aliphatic aldehydes having molecular weights from about 140 to about 200; aromatic aldehydes having molecular weights from about 90 to about 230; aliphatic and aromatic ethers having molecular weights from about 150 to about 270; and condensation products
- 25 of aldehydes and amines having molecular weights from about 180 to about 320; and essentially free from nitromusks and halogenated fragrance materials.

- More preferably, at least about 25%, more preferably at least about 50%, most preferably at least about 75%, by weight of the perfume is composed of fragrance material selected
- 30 from the group consisting of:

Common Name	Chemical Type	Chemical Name	Approx. M.W.
adoxal	aliphatic aldehyde	2,6,10-trimethyl-9-undecen-1-al	210
allyl amyl glycolate	ester	allyl amyl glycolate	182

allyl cyclohexane propionate	ester	allyl-3-cyclohexyl propionate	196
amyl acetate	ester	3-methyl-1-butanol acetate	130
amyl salicylate	ester	amyl salicylate	208
anisic aldehyde	aromatic aldehyde	4-methoxy benzaldehyde	136
aurantiol	schiff base	condensation product of methyl anthranilate and hydroxycitronellal	305
bacdanol	aliphatic alcohol	2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol	208
benzaldehyde	aromatic aldehyde	benzaldehyde	106
benzophenone	aromatic ketone	benzophenone	182
benzyl acetate	ester	benzyl acetate	150
benzyl salicylate	ester	benzyl salicylate	228
beta damascone	aliphatic ketone	1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	192
beta gamma hexanol	alcohol	3-hexen-1-ol	100
buccoxime	aliphatic ketone	1,5-dimethyl-oxime bicyclo[3,2,1] octan-8-one	167
cedrol	alcohol	octahydro-3,6,8,8-tetramethyl-1H-3A,7-methanoazulen-6-ol	222
cetalox	ether	dodecahydro-3A,6,6,9A-tetramethylnaphtho[2,1B]-furan	236
cis-3-hexenyl acetate	ester	cis-3-hexenyl acetate	142
cis-3-hexenyl salicylate	ester	beta, gamma-hexenyl salicylate	220
citronellol	alcohol	3,7-dimethyl-6-octenol	156
citronellyl nitrile	nitrile	geranyl nitrile	151
clove stem oil	natural		

coumarin	lactone	coumarin	146
cyclohexyl salicylate	ester	cyclohexyl salicylate	220
cymal	aromatic aldehyde	2-methyl-3-(para iso propyl phenyl)propionaldehyde	190
decyl aldehyde	aliphatic aldehyde	decyl aldehyde	156
delta damascone	aliphatic ketone	1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one	192
dihydromyrcenol	alcohol	3-methylene-7-methyl octan-7-ol	156
dimethyl benzyl carbinyl acetate	ester	dimethyl benzyl carbinyl acetate	192
ethyl vanillin	aromatic aldehyde	ethyl vanillin	166
ethyl-2-methyl butyrate	ester	ethyl-2-methyl butyrate	130
ethylene brassylate	macrocyclic lactone	ethylene tridecan-1,13-dioate	270
eucalyptol	aliphatic epoxide	1,8-epoxy-para-menthane	154
eugenol	alcohol	4-allyl-2-methoxy phenol	164
exaltolide	macrocyclic lactone	cyclopentadecanolide	240
flor acetate	ester	dihydro-nor-cyclopentadienyl acetate	190
florhydral	aromatic aldehyde	3-(3-isopropylphenyl) butanal	190
frutene	ester	dihydro-nor-cyclopentadienyl propionate	206
galaxolide	ether	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane	258
gamma decalactone	lactone	4-N-hepty-4-hydroxybutanoic acid lactone	170

gamma dodecalactone	lactone	4-N-octyl-4-hydroxy-butanoic acid lactone	198
geraniol	alcohol	3,7-dimethyl-2,6-octadien-1-ol	154
geranyl acetate	ester	3,7-dimethyl-2,6-octadien-1-yl acetate	196
geranyl nitrile	ester	3,7-dimethyl-2,6-octadienenitrile	149
helional	aromatic aldehyde	alpha-methyl-3,4, (methylenedioxy) hydrocinnamaldehyde	192
heliotropin	aromatic aldehyde	heliotropin	150
hexyl acetate	ester	hexyl acetate	144
hexyl cinnamic aldehyde	aromatic aldehyde	alpha-n-hexyl cinnamic aldehyde	216
hexyl salicylate	ester	hexyl salicylate	222
hydroxyambran	aliphatic alcohol	2-cyclododecyl-propanol	226
hydroxycitronellal	aliphatic aldehyde	hydroxycitronellal	172
ionone alpha	aliphatic ketone	4-(2,6,6-trimethyl-1-cyclohexenyl-1-yl)-3-buten-2-one	192
ionone beta	aliphatic ketone	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butene-2-one	192
ionone gamma methyl	aliphatic ketone	4-(2,6,6-trimethyl-2-cyclohexyl-1-yl)-3-methyl-3-buten-2-one	206
iso E super	aliphatic ketone	7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7,tetramethyl naphthalene	234
iso eugenol	ether	2-methoxy-4-(1-propenyl) phenol	164

iso jasmone	aliphatic ketone	2-methyl-3-(2-pentenyl)-2-cyclopenten-1-one	166
koavone	aliphatic aldehyde	acetyl di-isoamylene	182
lauric aldehyde	aliphatic aldehyde	lauric aldehyde	184
lavandin	natural		
lavender	natural		
lemon CP	natural	major component d-limonene	
d-limonene/orange terpenes	alkene	1-methyl-4-iso-propenyl-1-cyclohexene	136
linalool	alcohol	3-hydroxy-3,7-dimethyl-1,6-octadiene	154
linalyl acetate	ester	3-hydroxy-3,7-dimethyl-1,6-octadiene acetate	196
lrg 201	ester	2,4-dihydroxy-3,6-dimethyl benzoic acid methyl ester	196
lyral	aliphatic aldehyde	4-(4-hydroxy-4-methyl-pentyl) 3-cyclohexene-1-carboxaldehyde	210
majantol	aliphatic alcohol	2,2-dimethyl-3-(3-methylphenyl)-propanol	178
mayol	alcohol	4-(1-methylethyl) cyclohexane methanol	156
methyl anthranilate	aromatic amine	methyl-2-aminobenzoate	151
methyl beta naphthyl ketone	aromatic ketone	methyl beta naphthyl ketone	170
methyl cedrylone	aliphatic ketone	methyl cedrenyl ketone	246
methyl chavicol	ester	1-methoxy-4,2-propen-1-yl benzene	148
methyl dihydro jasmonate	aliphatic ketone	methyl dihydro jasmonate	226

methyl nonyl acetaldehyde	aliphatic aldehyde	methyl nonyl acetaldehyde	184
musk indanone	aromatic ketone	4-acetyl-6-tert butyl-1,1-dimethyl indane	244
nerol	alcohol	2-cis-3,7-dimethyl-2,6-octadien-1-ol	154
nonalactone	lactone	4-hydroxynonanoic acid, lactone	156
norlimbanol	aliphatic alcohol	1-(2,2,6-trimethyl-cyclohexyl)-3-hexanol	226
orange CP	natural	major component d-limonene	
P. T. buccinal	aromatic aldehyde	2-methyl-3(para tert butylphenyl) propionaldehyde	204
para hydroxy phenyl butanone	aromatic ketone	para hydroxy phenyl butanone	164
patchouli	natural		
phenyl acetaldehyde	aromatic aldehyde	1-oxo-2-phenylethane	120
phenyl acetaldehyde dimethyl acetal	aromatic aldehyde	phenyl acetaldehyde dimethyl acetal	166
phenyl ethyl acetate	ester	phenyl ethyl acetate	164
phenyl ethyl alcohol	alcohol	phenyl ethyl alcohol	122
phenyl ethyl phenyl acetate	ester	2-phenylethyl phenyl acetate	240
phenyl hexanol/phenoxanol	alcohol	3-methyl-5-phenylpentanol	178
polysantol	aliphatic alcohol	3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol	221
prenyl acetate	ester	2-methylbuten-2-ol-4-acetate	128
rosaphen	aromatic alcohol	2-methyl-5-phenyl pentanol	178

sandalwood	natural		
alpha-terpinene	aliphatic alkane	1-methyl-4-iso-propylcyclohexadiene-1,3	136
terpineol (alpha terpineol and beta terpineol)	alcohol	para-menth-1-en-8-ol, para-menth-1-en-1-ol	154
terpinyl acetate	ester	para-menth-1-en-8-yl acetate	196
tetra hydro linalool	aliphatic alcohol	3,7-dimethyl-3-octanol	158
tetrahydromyrcenol	aliphatic alcohol	2,6-dimethyl-2-octanol	158
tonalid/musk plus	aromatic ketone	7-acetyl-1,1,3,4,4,6-hexamethyl tetralin	258
undecalactone	lactone	4-N-heptyl-4-hydroxybutanoic acid lactone	184
undecavertol	alcohol	4-methyl-3-decen-5-ol	170
undecyl aldehyde	aliphatic aldehyde	undecanal	170
undecylenic aldehyde	aliphatic aldehyde	undecylenic aldehyde	168
vanillin	aromatic aldehyde	4-hydroxy-3-methoxybenzaldehyde	152
verdox	ester	2-tert-butyl cyclohexyl acetate	198
vertenex	ester	4-tert-butyl cyclohexyl acetate	198

and mixtures thereof.

When high initial perfume odor impact on fabrics is desired, it is also preferable to select  
5 a perfume containing perfume ingredients which are not too hydrophobic. The less hydrophobic perfume ingredients are more soluble in water, and are more available in composition. The degree of hydrophobicity of a perfume ingredient can be correlated with its octanol/water partitioning coefficient P. The octanol/water partitioning  
10 coefficient of a perfume ingredient is the ratio between its equilibrium concentration in octanol and in water. A perfume ingredient with a greater partitioning coefficient P is



more hydrophobic. Conversely, a perfume ingredient with a smaller partitioning coefficient  $P$  is more hydrophilic. The preferred perfume ingredients have an octanol/water partitioning coefficient  $P$  of about 1,000 or smaller. Since the partitioning coefficients of the perfume ingredients normally have high values, they are more  
5 conveniently given in the form of their logarithm to the base 10,  $\log P$ .

The  $\log P$  of many perfume ingredients has been reported; for example, the Pomona 92 database, available from Daylight Chemical Information Systems, Inc. (Daylog CIS), Irvine, California, contains many, along with citations to the original literature. However,  
10 the  $\log P$  values are most conveniently calculated by the "CLOG P" program, also available from Daylight CIS. This program also lists experimental  $\log P$  values when they are available in the Pomona 92 database. The "calculated  $\log P$ " (Clog P) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p.  
15 295, Pergamon Press, 1990). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The Clog P values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental  $\log P$  values in the selection of perfume ingredients which are useful in the  
20 present invention.

When hydrophilic perfume is desired, at least about 25% by weight of the perfume, more preferably about 50%, most preferably about 75%, is composed of perfume ingredients having a Clog P of about 3 or smaller.

25

### Cyclodextrin

The compositions herein can also contain a cyclodextrin. As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin,  
30 beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in a donut-shaped ring. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structure with a hollow interior of a specific  
35 volume. The "lining" of the internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms, therefore this surface is fairly hydrophobic. The unique shape

and physical-chemical property of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many perfume molecules can fit into the cavity.

- 5 Preferred cyclodextrins are highly water-soluble such as, alpha-cyclodextrin and derivatives thereof, gamma-cyclodextrin and derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated  
10 cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a  $-\text{CH}_2\text{-CH(OH)-CH}_3$  or a  $-\text{CH}_2\text{CH}_2\text{-OH}$  group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3(dimethylamino)propyl ether, wherein  
15 R is  $\text{CH}_2\text{-CH(OH)-CH}_2\text{-N(CH}_3)_2$  which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is  $\text{CH}_2\text{-CH(OH)-CH}_2\text{-N}^+(\text{CH}_3)_3\text{Cl}^-$ ; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins  
20 wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, and mixtures thereof. Other cyclodextrin derivatives are disclosed in US-A-3,426,011, US-A-3,453,257, US-A-  
25 3,453,258, US-A-3,453,259, US-A-3,453,260, US-A-3,459,731, US-A-3,553,191, US-A-3,565,887, US-A-4,535,152, US-A-4,616,008, US-A-4,678,598, US-A-4,638,058, and US-A-4,746,734.

- Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g  
30 in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin, methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl  
35 cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per

cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- $\beta$ -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2  
5 methyl groups with a degree of substitution of about 14. A preferred, more commercially available methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin having a degree of substitution of about 12.6. The preferred cyclodextrins are available, e.g., from American Maize-Products Company and Wacker Chemicals (USA), Inc.

#### 10 Metallic odor-control salts

The compositions herein can also contain a metallic salt, preferably a water-soluble salt selected from zinc salts, copper salts and mixtures thereof, as an odor control agent and to absorb amine and sulfur-containing compounds. Examples of preferred water-soluble  
15 zinc salts are zinc chloride, zinc gluconate, zinc lactate, zinc maleate, zinc salicylate, zinc sulfate, etc. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Examples of preferred copper salts are copper chloride and copper gluconate. See also US-A-4,325,939, US-A-4,469,674, and US-A-3,172,817

#### Astringent metallic salts

20 Astringent metallic salts are suitable for use as antiperspirant materials, especially the inorganic and organic salts of aluminum, zirconium, and zinc, and mixtures thereof. Particularly preferred are the aluminum and zirconium salts such as aluminum halides, aluminum hydroxy halides, zirconyl oxide halides, and zirconyl hydroxy halides, and complexes of aluminum, zirconium, and/or zinc with amino acids, e.g., glycines.  
25 Specific, exemplary aluminum salts that can be used include aluminum chloride and aluminum hydroxyhalides such as the aluminum chlorhydroxides referred to as "5/6 basic chlorhydroxide" and "2/3 basic chlorhydroxide". Aluminum salts of this type can be prepared in the manner described more fully in US-A-3,887,692, US-A-3,904,741, US-A-4,359,456, and GB-A-2,048,229.

30

#### Solubilizing Aid

The compositions herein can also contain a solubilizing aid. A suitable solubilizing aid is surfactant, preferably a no-foaming or low-foaming surfactant. Suitable surfactants are nonionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants,  
35 and mixtures thereof, preferably nonionic surfactants and cationic surfactants, and mixtures thereof. Suitable surfactants can be emulsifiers and/or deterative surfactants.

Mixtures of emulsifiers and deterative surfactants are also preferred. When a surfactant containing one, or more, alkyl group is used, it is preferred that it contain relatively short alkyl chains of from about 5 to about 14 carbon atoms. Typical nonionic surfactants are polyethylene glycol-polypropylene glycol block copolymers, such as Pluronic® and Pluronic R® surfactants from BASF; Tetronic® and Tetronic R® surfactants from BASF, ethoxylated branched aliphatic diols, such as Surfynol® surfactants from Air Products; ethoxylated alkyl phenols, such as Igepal® surfactants from Rhône-Poulenc; ethoxylated aliphatic alcohols and carboxylic acids; polyethylene glycol diesters of fatty acids; and mixtures thereof. Preferably, said solubilizing aid is a nonionic surfactant selected from the group consisting of fatty acid esters of ethoxylated sorbitans. More preferably said solubilizing aid is selected from the group consisting of mixtures of laurate esters of sorbitol and sorbitol anhydrides; mixtures of stearate esters of sorbitol and sorbitol anhydrides; and mixtures of oleate esters of sorbitol and sorbitol anhydrides. Even more preferably said solubilizing aid is selected from the group consisting of Polysorbate 20, which is a mixture of laurate esters of sorbitol and sorbitol anhydrides consisting predominantly of the monoester, condensed with about 20 moles of ethylene oxide; Polysorbate 60 which is a mixture of stearate esters of sorbitol and sorbitol anhydride, consisting predominantly of the monoester, condensed with about 20 moles of ethylene oxide; Polysorbate 80 which is a mixture of oleate esters of sorbitol and sorbitol anhydrides, consisting predominantly of the monoester, condensed with about 20 moles of ethylene oxide; and mixtures thereof. Most preferably, said solubilizing aid is Polysorbate 60. Preferred cationic surfactants are di(C<sub>8</sub>-C<sub>12</sub> alkyl)di(C<sub>1</sub>-C<sub>2</sub> alkyl)ammonium halides, alkylbenzyltrimethylammonium halides, amine oxides, and mixtures thereof. Preferred amphoteric surfactants are the betaines. It is preferred that the surfactant have good wetting properties. Also preferred are surfactants that have the hydrophilic groups between hydrophobic chains, such as, Pluronic R surfactants, Surfynol surfactants, polyethylene glycol diesters of fatty acids, fatty acid esters of ethoxylated sorbitans, di(C<sub>8</sub>-C<sub>12</sub> alkyl)di(C<sub>1</sub>-C<sub>2</sub> alkyl)ammonium halides, and mixtures thereof; surfactants that have hydrophilic groups situated at the extremities of the hydrophobic chain, such as Pluronic surfactants; and mixtures thereof. Mixtures of these surfactants and other types of surfactants are also preferred to form no-foaming or low-foaming solubilizing agents. Polyalkylene glycol can be used as defoaming agent in combination with the solubilizing agents.

When a solubilizing aid is used in the composition of the present invention, more specifically when fatty acid esters of ethoxylated sorbitans are used as the solubilizing

aid, it is preferable to use the process of high shear milling in order aid in the incorporation of excess hydrophobic organic material.

#### Aqueous Liquid Carrier

5 Aqueous liquid carriers can include water, organic solvents, etc. Preferred aqueous carriers contain water in at least about 50% by weight thereof. The water used can be distilled, deionized, or tap water. Water containing a small amount of low molecular weight monohydric alcohols, e.g., ethanol, methanol, and isopropanol, or polyols, such as ethylene glycol and propylene glycol, can also be useful. However, the volatile low  
10 molecular weight monohydric alcohols such as ethanol and/or isopropanol should be limited since these volatile organic compounds will contribute both to flammability problems and environmental pollution problems. Other suitable solvents include carbitol, acetone and dimethoxymethane;

#### Hydrophobic Liquid Carrier

15 The compositions of this invention can also contain a hydrophobic liquid carrier. Suitable hydrophobic liquids include fatty acid and fatty alcohol esters, water-insoluble ethers and alcohols, polyorgano silicones, propellants and mixtures thereof. Such hydrophobic liquids are disclosed in US-A-4,053,851, US-A-4,065,564, US-A-4,073,880, US-A-  
20 4,278,655, and GB-A-2,018,590. Silicones and propellants are described in more detail below.

#### Propellants

Propellants suitable for use in aerosol compositions can be any liquefiable gas  
25 conventionally used for aerosol containers. Preferably the relative density of the propellant or mixture thereof is less than 1 so that pure propellant is not emitted from the container. Examples of materials suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethylether e.g Dimel 152A  
30 (RTM) supplied by Du Pont, propane, n-butane, isobutane, used singly or admixed and propane butane e.g CAP 80 (RTM). Dimel 152A (RTM) and propane butane are preferred.

#### Preservatives

35 Antimicrobial preservatives useful herein can be biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate

the growth of microorganisms. The preservative can be any organic preservative material which will not cause damage to substrates, e.g., discoloration, coloration, bleaching. Preferred water-soluble preservatives include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary compounds, dehydroacetic acid, phenyl and phenoxy compounds, and mixtures thereof.

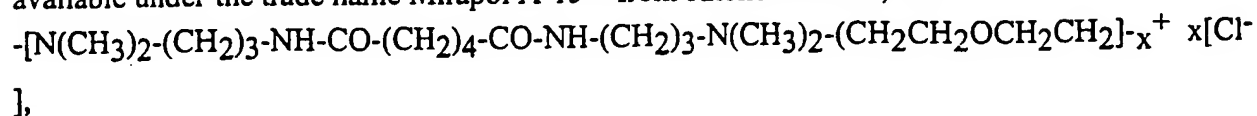
Non-limiting examples of water-soluble preservatives include a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum preservative available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Co.; 5-bromo-5-nitro-1,3-dioxane, available under the trade name Bronidox L® from Henkel; 2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol® from Inolex; 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and digluconic acids; a 95:5 mixture of 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione and 3-butyl-2-iodopropynyl carbamate, available under the trade name Glydant Plus® from Lonza; N-[1,3-bis(hydroxymethyl)2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxy-methyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall II® from Sutton Laboratories, Inc.; N,N"-methylenebis{N'-[1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol® from 3V-Sigma, Unicide U-13® from Induchem, Germall 115® from Sutton Laboratories, Inc.; polymethoxy bicyclic oxazolidine, available under the trade name Nuosept® C from Hüls America; formaldehyde; glutaraldehyde; polyaminopropyl biguanide; available under the trade name Cosmocil CQ® from ICI Americas, Inc., or under the trade name Mikrokill® from Brooks, Inc; dehydroacetic acid; and mixtures thereof.

#### Antistatic Agents

The composition herein can also contain an antistatic agent, preferably a water-soluble antistatic agent. Examples include monoalkyl cationic quaternary ammonium compounds, e.g., mono(C<sub>10</sub>-C<sub>14</sub> alkyl)trimethyl ammonium halide, such as monolauryl trimethyl ammonium chloride, hydroxycetyl hydroxyethyl dimethyl ammonium chloride, available under the trade name Dehyquart E® from Henkel, and ethyl bis(polyethoxy ethanol) alkylammonium ethylsulfate, available under the trade name Variquat 66® from Witco Corp., polyethylene glycols, polymeric quaternary ammonium salts, such as polymers conforming to the general formula:



available under the trade name Mirapol A-15<sup>®</sup> from Rhône-Poulenc, and



available under the trade name Mirapol AD-1<sup>®</sup> from Rhône-Poulenc, quaternized polyethyleneimines, vinylpyrrolidone/methacrylamidopropyltrimethylammonium chloride copolymer, available under the trade name Gafquat HS-100<sup>®</sup> from GAF;

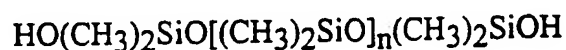
triethonium hydrolyzed collagen ethosulfate, available under the trade name Quat-Pro E<sup>®</sup> from Maybrook; and mixtures thereof.

### Silicones

Silicones suitable for use herein are water-insoluble and include non-volatile polyalkyl and polyaryl siloxane gums and fluids, volatile cyclic and linear polyalkylsiloxanes, polyalkoxylated silicones, amino and quaternary ammonium modified silicones, rigid cross-linked and reinforced silicones and mixtures thereof.

Silicone gums generally have a molecular weight of from about 200,000 to about 4,000,000 and include dimethiconol, fluorosilicone and dimethicone and mixtures thereof. Mixtures of silicone gums and silicone-based carriers having a viscosity from about 0.65 mm<sup>2</sup>.s<sup>-1</sup> to about 100 mm<sup>2</sup>.s<sup>-1</sup> in a gum:carrier ratio of from about 10:90 to about 20:80 are also suitable.

Dimethiconol-based silicones have the chemical structure (II):



where n is from about 2000 to about 40,000, preferably from about 3000 to about 30,000.

Examples of dimethiconol-based silicones includes Dow Corning Q2-1403 (85% 5 mm<sup>2</sup>.s<sup>-1</sup> Dimethicone Fluid/15% Dimethiconol) and Dow Corning Q2-1401.

The fluorosilicones useful herein have a molecular weight of from about 200,000 to about 300,000, preferably from about 240,000 to about 260,000 and most preferably about 250,000.

The silicone gums include dimethicones as described by Petrarch and others including US-A-4,152,416, May 1, 1979 to Spitzer, et al, and Noll, Walter, Chemistry and Technology of

Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. "Silicone gum" materials denote high molecular weight materials having a mass-average molecular weight in excess of about 200,000 and preferably from about 200,000 to about 4,000,000. Typically, they have a  
5 viscosity at 25°C in excess of about 1,000,000 mm<sup>2</sup>.s<sup>-1</sup>. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl) (methylvinylsiloxane) copolymer and mixtures thereof.

10 Silicone fluids suitable for use herein include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers and mixtures thereof.

The polyalkyl siloxane fluids that can be used include, for example, polydimethylsiloxanes with viscosities ranging from about 0.65 to 600,000 mm<sup>2</sup>.s<sup>-1</sup>, preferably from about 0.65 to about 10,000 mm<sup>2</sup>.s<sup>-1</sup> at 25°C. These siloxanes are available, for example, from the General Electric  
15 Company as the Viscasil (RTM) series and from Dow Corning as the Dow Corning 200 series. The essentially non-volatile polyalkylarylsiloxane fluids that can be used include, for example, polymethylphenylsiloxanes, having viscosities of about 0.65 to 30,000 mm<sup>2</sup>.s<sup>-1</sup> at 25°C. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

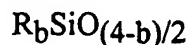
20 The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 29, 1970.

Also suitable for use herein are certain volatile cyclic and linear polydimethylsiloxanes. As used  
25 herein, "volatile" refers to those materials which have a measurable vapor pressure at ambient conditions. Such volatile silicone oils may be cyclic or linear. A description of volatile silicone oils is found in Todd, et al., "Volatile Silicone Fluids for Cosmetics", 91 Cosmetics and Toiletries, 27-32 (1976). Preferred volatile silicone oils include those having from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 5 silicon atoms. Cyclic  
30 volatile silicones useful herein generally contain from about 3 to about 7 silicon atoms while linear volatile silicones contain from about 3 to about 9 silicon atoms. Linear volatile silicones generally have viscosities of less than about 5 centistokes at 25 °C., whereas the cyclic silicones have viscosities of less than about 10 centistokes at 25 °C. Examples of volatile silicone oils useful herein include: Dow Corning 344, Dow Corning 345 and Dow Corning 200 (sold by Dow  
35 Corning Corporation); 7207 and 7158 (sold by General Electric Company); and SWS-03314 (sold by SWS Silicones Corporation).



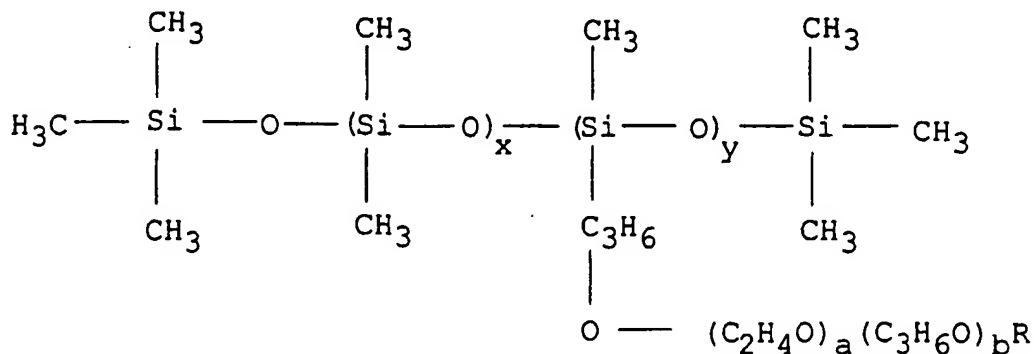
Another class of silicone component suitable for use herein include polydiorganosiloxane-polyoxyalkylene copolymers containing at least one polydiorganosiloxane segment and at least one polyoxyalkylene segment, said polydiorganosiloxane segment consisting essentially of

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siloxane units wherein b has a value of from about 0 to about 3, inclusive, there being an average value of approximately 2 R radicals per silicon for all siloxane units in the copolymer, and R denotes a radical selected from methyl, ethyl, vinyl, phenyl and a divalent radical bonding said polyoxyalkylene segment to the polydiorganosiloxane segment, at least about 95% of all R radicals being methyl; and said polyoxyalkylene segment having an average molecular weight of at least about 1000 and consisting of from about 0 to about 50 mol percent polyoxypropylene units and from about 50 to about 100 mol percent polyoxyethylene units, at least one terminal portion of said polyoxyalkylene segment being bonded to said polydiorganosiloxane segment, any terminal portion of said polyoxyalkylene segment not bonded to said polydiorganosiloxane segment being satisfied by a terminating radical; the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in said copolymer having a value of from about 2 to about 8. Such polymers are described in US-A-4,268,499.

Preference for use herein are polydiorganosiloxane-polyoxyalkylene copolymers having the general formula:



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wherein x and y are selected such that the weight ratio of polydiorgano-siloxane segments to polyoxalkalkylene segments is from about 2 to about 8, the mol ratio of a:(a+b) is from about 0.5 to about 1, and R is a chain terminating group, especially selected from hydrogen; hydroxyl; alkyl, such as methyl, ethyl, propyl, butyl, benzyl; aryl, such as phenyl; alkoxy such as methoxy, ethoxy, propoxy, butoxy; benzyloxy; aryloxy, such as phenoxy; alkynyloxy, such as vinyloxy and allyloxy; acyloxy, such as acetoxo, acryloxy and propionoxy and amino, such as dimethylamino.

The number of and average molecular weights of the segments in the copolymer are such that the weight ratio of polydiorganosiloxane segments to polyoxyalkylene segments in the copolymer is preferably from about 2.5 to about 4.0.

Suitable copolymers are available commercially under the tradenames Belsil (RTM) from Wacker-Chemie GmbH, Geschäftsbereich S, Postfach D-8000 Munich 22 and Abil (RTM) from Th. Goldschmidt Ltd., Tego House, Victoria Road, Ruislip, Middlesex, HA4 0YL. Particularly preferred for use herein are Belsil (RTM) 6031 and Abil (RTM) B88183.

The above polydiorganosiloxane - polyoxyalkylene copolymers can be used above or in admixture with other silicones, for example, the volatile cyclic polydimethylsiloxanes. Moreover, such copolymers and mixtures can be used in combination with the herein defined silicone gums.

#### Suspending Agents

Suspending agents herein include colloidal silicas such as Cab-O-Sil (RTM), a submicroscopic, particulated pyrogenic silica, and clays and hydrophobically-treated clays. Suitable clays include montmorillonite clays, e.g., bentonites and hectorites and colloidal magnesium aluminum silicates. Many such clay suspension agents are commercially available. They include, for example, Bentone 38 (hectorite) and Bentone 34 (bentonite) sold by NL Industries, Inc., Laponite (hectorite) marketed by Laporte Industries, Ltd., and Tixogel (bentonite) sold by United Catalyst, Inc. The magnesium aluminum silicates are complexes of colloidal magnesium aluminum silicate richer in magnesium than aluminum. Magnesium aluminum silicates are commercially available as Veegum (R. T. Vanderbilt Co.). The hectorite and bentonite clay minerals can be described as expandable (swellable), three-layer clays, in which a sheet of aluminum/oxygen atoms or magnesium/oxygen atoms lies between two layers of silicone/oxygen atoms, i.e., aluminosilicates and magnesium silicates, having an ion

exchange capacity of at least about 50 meq/100 . of clay, and preferably at least about 60 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the ayered clay structure to be swollen or expanded on contact with water. Such hectorite and bentonite clays are described in Grim, Clay Mineralogy (2nd. Ed.) pp. 77-79 (1968), and in Van Olphen, An Introduction to Clay colloid Chemistry, (2nd Ed.) pp 64-76 (1977). The clay minerals can contain exchangeable cations including, but not limited to, protons, sodium ions, potassium ions, calcium ions, magnesium ions, lithium ions, and the like.

10 The clay minerals are made hydrophobic by treating them with a cationic surfactant material. A preferred cationic surfactant is a quaternary ammonium cationic surfactant. A particularly preferred cationic surfactant is ditallow dimethyl ammonium chloride (e.g., quaternium-18).

15 Preferred clay suspension agents include hydrophobically treated montmorillonite clays, e.g., hydrophobic bentonites available under the tradename of Bentone. Bentone is prepared by reacting bentonite in a cation exchange system with an amine. Specific examples of Bentones are Bentone 38, Bentone 34, Bentone 27, Bentone 14, and Bentone LT, all of which have a particle size of below about 5 microns and are commercially  
20 available from the NL Industries, Inc.

The suspension agent can also be used in conjunction with an activator such as propylene carbonate, ethanol, and mixtures thereof.

#### 25 Insect and/or Moth Repelling Agent

The compositions herein can also contain an insect and/or moth repelling agents. Typical insect and moth repelling agents are pheromones, such as anti-aggregation pheromones, and other natural and/or synthetic ingredients. Preferred insect and moth repellent agents useful in the composition of the present invention are perfume ingredients, such as  
30 citronellol, citranellal, citral, linalool, cedar extract, geranium oil, sandalwood oil, 2-(diethylphenoxy)ethanol, 1-dodecene, etc. Other examples of insect and/or moth repellents useful in the composition of the present invention are disclosed in U.S. Pat. Nos. 4,449,987, 4,693,890, 4,696,676, 4,933,371, 5,030,660, 5,196,200, and in "Semio Activity of Flavor and Fragrance Molecules on Various Insect Species", B.D. Mookherjee  
35 et al., published in Bioactive Volatile Compounds from Plants, ASC Symposium Series

525, R. Teranishi, R.G. Buttery, and H. Sugisawa, 1993, pp. 35-48, all of said patents and publications incorporated herein by reference.

### Colorant

5 Colorants and dyes, especially bluing agents, can also be added herein for visual appeal and performance impression. When colorants are used, they are used at extremely low levels to avoid fabric staining. Preferred colorants for use in the present compositions are highly water-soluble dyes, e.g., Liquitint® dyes available from Milliken Chemical Co. Non-limiting examples of suitable dyes are, Liquitint Blue HP®, Liquitint Blue 65®,  
10 Liquitint Patent Blue®, Liquitint Royal Blue®, Liquitint Experimental Yellow 8949-43®, Liquitint Green HMC®, Liquitint Yellow II®, and mixtures thereof, preferably Liquitint Blue HP®, Liquitint Blue 65®, Liquitint Patent Blue®, Liquitint Royal Blue®, Liquitint Experimental Yellow 8949-43®, and mixtures thereof.

### 15 Spray Dispenser

Spray dispensers can be any of the manually activated means for producing a spray of liquid droplets as is known in the art, e.g. trigger-type, pump-type, non-aerosol self-pressurized, and aerosol-type spray means.

20 The spray dispenser can be an aerosol dispenser. Said aerosol dispenser comprises a container which can be constructed of any of the conventional materials employed in fabricating aerosol containers. The dispenser must be capable of withstanding internal pressure in the range of from about 20 to about 110 p.s.i.g., more preferably from about 20 to about 70 p.s.i.g. The one important requirement concerning the dispenser is that it  
25 be provided with a valve member which will permit the composition contained in the dispenser to be dispensed in the form of a spray of very fine, or finely divided, particles or droplets. The aerosol dispenser utilizes a pressurized sealed container from which the composition is dispensed through a special actuator/valve assembly under pressure. The aerosol dispenser is pressurized by incorporating therein a gaseous component generally  
30 known as a propellant. Common aerosol propellants, e.g., gaseous hydrocarbons such as isobutane, and mixed halogenated hydrocarbons, are not preferred. Halogenated hydrocarbon propellants such as chlorofluoro hydrocarbons have been alleged to contribute to environmental problems. Preferred propellants are compressed air, nitrogen, inert gases, carbon dioxide, etc. A more complete description of commercially available  
35 aerosol-spray dispensers appears in US-A-3,436,772, and US-A-3,600,325.

Preferably the spray dispenser can be a self-pressurized non-aerosol container having a convoluted liner and an elastomeric sleeve. Said self-pressurized dispenser comprises a liner/sleeve assembly containing a thin, flexible radially expandable convoluted plastic liner of from about 0.010 to about 0.020 inch thick, inside an essentially cylindrical elastomeric sleeve. The liner/sleeve is capable of holding a substantial quantity of odor-absorbing fluid product and of causing said product to be dispensed. A more complete description of self-pressurized spray dispensers can be found in US-A-5,111,971 and US-A-5,232,126. Another type of aerosol spray dispenser is one wherein a barrier separates the composition from the propellant (preferably compressed air or nitrogen), as disclosed in US-A-4,260,110. Such a dispenser is available from EP Spray Systems, East Hanover, New Jersey.

More preferably, the spray dispenser is a non-aerosol, manually activated, pump-spray dispenser. Said pump-spray dispenser comprises a container and a pump mechanism which securely screws or snaps onto the container. The container comprises a vessel for containing the composition to be dispensed.

The pump mechanism comprises a pump chamber of substantially fixed volume, having an opening at the inner end thereof. Within the pump chamber is located a pump stem having a piston on the end thereof disposed for reciprocal motion in the pump chamber. The pump stem has a passageway there through with a dispensing outlet at the outer end of the passageway and an axial inlet port located inwardly thereof.

The container and the pump mechanism can be constructed of any conventional material employed in fabricating pump-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyethyleneterephthalate; blends of polyethylene, vinyl acetate, and rubber elastomer. A preferred container is made of clear, e.g., polyethylene terephthalate. Other materials can include stainless steel. A more complete disclosure of commercially available dispensing devices appears in US-A- 4,895,279, US-A-4,735,347, and US-A-4,274,560.

Most preferably, the spray dispenser is a manually activated trigger-spray dispenser. Said trigger-spray dispenser comprises a container and a trigger both of which can be constructed of any of the conventional material employed in fabricating trigger-spray dispensers, including, but not limited to: polyethylene; polypropylene; polyacetal; polycarbonate; polyethyleneterephthalate; polyvinyl chloride; polystyrene; blends of

polyethylene, vinyl acetate, and rubber elastomer. Other materials can include stainless steel and glass. A preferred container is made of clear, e.g. polyethylene terephthalate. The trigger-spray dispenser does not incorporate a propellant gas into the odor-absorbing composition, and preferably it does not include those that will foam the odor-absorbing composition. The trigger-spray dispenser herein is typically one which acts upon a discrete amount of the composition itself, typically by means of a piston or a collapsing bellows that displaces the composition through a nozzle to create a spray of thin liquid. Said trigger-spray dispenser typically comprises a pump chamber having either a piston or bellows which is movable through a limited stroke response to the trigger for varying the volume of said pump chamber. This pump chamber or bellows chamber collects and holds the product for dispensing. The trigger spray dispenser typically has an outlet check valve for blocking communication and flow of fluid through the nozzle and is responsive to the pressure inside the chamber. For the piston type trigger sprayers, as the trigger is compressed, it acts on the fluid in the chamber and the spring, increasing the pressure on the fluid. For the bellows spray dispenser, as the bellows is compressed, the pressure increases on the fluid. The increase in fluid pressure in either trigger spray dispenser acts to open the top outlet check valve. The top valve allows the product to be forced through the swirl chamber and out the nozzle to form a discharge pattern. An adjustable nozzle cap can be used to vary the pattern of the fluid dispensed.

For the piston spray dispenser, as the trigger is released, the spring acts on the piston to return it to its original position. For the bellows spray dispenser, the bellows acts as the spring to return to its original position. This action causes a vacuum in the chamber. The responding fluid acts to close the outlet valve while opening the inlet valve drawing product up to the chamber from the reservoir.

A more complete disclosure of commercially available dispensing devices appears in US-A-4,082,223, US-A-4,434,917, and US-A-4,819,835.

A broad array of trigger sprayers or finger pump sprayers are suitable for use with the compositions of this invention. These are readily available from suppliers such as Calmar, Inc., City of Industry, California; CSI (Continental Sprayers, Inc.), St. Peters, Missouri; Berry Plastics Corp., Evansville, Indiana—a distributor of Guala® sprayers; or Seaquest Dispensing, Cary, Illinois.

- The preferred trigger sprayers are the blue inserted Guala® sprayer, available from Berry Plastics Corp., or the Calmar TS800-1A sprayers, available from Calmar Inc., because of the fine uniform spray characteristics, spray volume, and pattern size. Any suitable bottle or container can be used with the trigger sprayer, the preferred bottle is a 17 fl-oz. bottle
- 5 (about 500 ml) of good ergonomics similar in shape to the Cinch® bottle. It can be made of any materials such as high density polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyethylene terephthalate, glass, or any other material that forms bottles. Preferably, it is made of high density polyethylene or clear polyethylene terephthalate.
- 10 For smaller four fl-oz. size (about 118 ml), a finger pump can be used with canister or cylindrical bottle. The preferred pump for this application is the cylindrical Euromist II®, from Sequest Dispensing.

What is claimed is:

- 5 1. Use of a large pore phosphate-containing molecular sieve having a pore diameter of at least about 5 Angstroms as agent for the control of odors.
2. Use according to claim 1 wherein the odor-control agent is selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and  
10 metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn.
3. A method of controlling the odor of an animate or inanimate object comprising treating the object with a composition comprising an odor-control agent selected from  
15 large pore phosphate-containing molecular sieves having a pore diameter of at least about 5 Angstroms.
4. A method according to claim 3 wherein the odor-control agent is selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and  
20 metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn.
5. An odor-control composition comprising an odor-control agent selected from large pore phosphate-containing molecular sieves having a pore diameter of at least about 5  
25 Angstroms together with a carrier therefor.
6. A composition according to claim 5 in the form of a particulate solid, liquid, gel or aerosol.
- 30 7. A composition according to claim 5 or 6 wherein the odor-control agent is selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn.
- 35 8. A composition according to any of claims 5 to 7 wherein the phosphate-containing molecular sieve has a pore diameter of greater than about 10 Angstroms.



9. A composition according to any of claims 5 to 8 additionally comprising a mesoporous molecular sieve having a pore diameter of at least 13, preferably at least 15, more preferably at least 20 Angstroms.

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10. A composition according to claim 9 wherein the mesoporous molecular sieve consists essentially of crystalline, inorganic material exhibiting after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least 18 Angstroms.

- 10 11. A composition according to claim 10 wherein the mesoporous molecular sieve consists essentially of inorganic, porous, crystalline material having, after calcination, a hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units.

15

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/23154

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L9/014

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L C10G B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 91 12030 A (PROCTER & GAMBLE) 22 August 1991 (1991-08-22) abstract page 1, line 4-11 page 7, line 13 page 11, line 6,28-32 page 14, line 14-37 ---	1-8
A	US 4 683 217 A (LOK BRENT M ET AL) 28 July 1987 (1987-07-28) abstract column 3, line 49-55,66-68 --- -/--	1-5,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 January 2000

Date of mailing of the international search report

04/02/2000

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Böhm, I

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/US 99/23154

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 407 422 A (MATTHIJS OMER ET AL) 18 April 1995 (1995-04-18) abstract; example 9 column 4, line 57-68 column 6, line 30-34,50 column 7, line 6-9 column 8, line 47 -column 9, line 3 column 10, line 44-46 ----	1,3,5,6
A	US 4 437 429 A (ABREVAYA ALBERT ET AL) 20 March 1984 (1984-03-20) abstract column 3, line 55-61 ----	1,3,5,6
A	US 4 793 833 A (LOK BRENT M T ET AL) 27 December 1988 (1988-12-27) abstract column 1, line 10-68 column 2, line 58-67 ----	1,2,5,7
A	US 5 378 440 A (HERBST JOSEPH A ET AL) 3 January 1995 (1995-01-03) cited in the application abstract column 8, line 14-34 -----	1,5,9-11

# INTERNATIONAL SEARCH REPORT

information on patent family members

Inte. onal Application No

PCT/US 99/23154

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9112030	A	22-08-1991	AT 128630 T	15-10-1995
			AU 658137 B	06-04-1995
			AU 7309291 A	03-09-1991
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			DK 515503 T	12-02-1996
			EG 19133 A	30-08-1994
			EP 0515503 A	02-12-1992
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